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**(54) Adhesive blends for polystyrene and composite structures made therefrom**

(57) Adhesive blends having special utility in the formation of composite structures with LDPE, EVOH, and impact-modified polystyrene comprise a mixture of an ethylene/ester copolymer such as EVA, polystyrene, such as impact-modified polystyrene, and a functionalized SEBS block copolymer.

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## Description

The invention relates generally to adhesive blends and composite structures made therefrom and, more particularly, the invention relates to adhesive blends useful in adhering to polyolefin, polar and polystyrene substrates useful in food packaging and related applications.

There has long been a perceived need for laminate structures comprising one or more of a food contact or sealing layer, a barrier layer, and a structural layer for use in the packaging and storage of food. Food contact/sealing layers often comprise non-polar polyolefins such as low density polyethylene (LDPE), for example, while typical barrier layers comprise substrates of polymers such as ethylene vinyl alcohol (EVOH), for example. Structural layers may comprise styrene polymers, which may contain rubber. High impact polystyrene (HIPS) is especially attractive as a structural layer, given its attractive physical properties, ease of extrusion processing, thermoforming, and cutting.

Such composite structures are useful as semi-rigid food packaging (e.g. thermoformed cups) or cast or blown film useful for packaging meat or cheese. Another application is in the fabrication of refrigerator liners that must form a good barrier against hydrohalocarbon blowing agent penetration that can lead to loss of refrigerant and solvent induced stress loading of various polymers.

It is desirable to form such structures by coextrusion or another method wherein a tie layer of adhesive is sandwiched between adjacent, often diverse substrates. Given the diversity of substrates useful in a laminate structure, however, one problem in the past has been to provide an adhesive tie layer which gives acceptable adhesion to each of the substrates present in the structure while being easily processable (i.e., thermoformable, readily die cut, etc.) without permanently changing form after thermoforming. For example, some adhesives remain soft or stringy after thermoforming, compromising the ease of processing by die cutting.

Adhesives useful in this type of composite structure must also be approved by the U.S. Food and Drug Administration or the European Economic Community regulatory authority which approves such materials for use in food packaging.

The present invention is directed to an adhesive blend, comprising a mixture of an ethylene/ester copolymer, polystyrene, and a functionalized styrene-ethylene/butylene-styrene (SEBS) block copolymer.

The present invention is further directed to a composite structure comprising the adhesive blend of the present invention adhered to a substrate.

According to the invention, adhesive blend useful in adhering to a wide variety of substrates including non-polar polyolefins, polar substrates, and polystyrene is formed from a mixture of an ethylene/ester copolymer, polystyrene, and a functionalized styrene/rubber containing copolymer. In a preferred form, the adhesive blend comprises a mixture of an ethylene/vinyl acetate copolymer, impact-modified polystyrene, and a grafted SEBS block copolymer.

The invention also provides composite structures comprising the inventive adhesive blend adhered to one or more substrates.

Other objects and advantages of the invention will be apparent to those skilled in the art from a review of the following detailed description taken in conjunction with the appended claims.

The adhesive blends of the invention generally comprise mixtures of an ethylene/ester copolymer, polystyrene, and a functionalized SEBS block copolymer. The adhesive blends can contain fillers, stabilizers, antioxidants, colorants, etc. or other additional components such as SEBS, SBS, or SIS elastomers or styrene-rubber materials, which may act as compatibilizers to enhance adhesion characteristics.

In various forms, the inventive adhesive blends may consist essentially of consist of the three essential components identified above, exclusive of antioxidant packages or other additives.

The ethylene/ester copolymer component may comprise a copolymer of ethylene with any of the wide variety of esters such as vinyl acetate or acrylates such as methyl acrylate and n-butyl acrylate, for example. Preferably, the ethylene/ester copolymer comprises an ethyl/vinyl acetate (EVA) copolymer comprising about 5 wt.% to about 40 wt% vinyl acetate, preferably about 18 wt.% to about 28 wt.% vinyl acetate. High levels of vinyl acetate are preferred; 28% vinyl acetate EVAs are particularly preferred. An example of a commercially available EVA suitable for use in the invention is that sold by Quantum Chemical Company (Cincinnati, Ohio) under the trade designation UE 634-04. This product contains about 28 wt.% vinyl acetate.

The polystyrene component may be grafted or ungrafted, and may comprise any of a variety of crystalline polystyrenes or so-called impact-modified polystyrenes such as those conventionally referred to as "high impact" polystyrenes ("HIPS"). Impact-modified polystyrene is preferred.

Preferably, the polystyrene is impact-modified by an elastomer such as a polybutadiene elastomer or a polybutadiene-styrene elastomer. It can be prepared by post-reactor blending of the polystyrene and elastomer components, or by *in situ* polymerization of styrene monomer and an unsaturated rubber (e.g., polybutadiene or styrene-butadiene elastomer). In the latter case, a physical blend and graft copolymers of the components may be present. Generally, the polystyrene is a high molecular weight polymer, having a molecular weight greater than about 50,000.

The synthesis and characterization of high impact polystyrene is described in detail in *Encyclopedia of Polymer Science and Engineering* (John Wiley & Sons, New York, 1989), Vol. 16, pp. 88-97, the disclosure of which is hereby incorporated by reference.

Typically, useful HIPS materials will have a melt index as measured according to ASTM D-1238, Condition G (200°C, 5000 g) of about 0.5 g/10 min to about 12 g/10 min highly preferably about 2 g/10 min to about 4 g/10 min. Preferably, the notched Izod impact (73°F) of such materials according to ASTM D-256 will be greater than 0.5 ft-lb/in and highly preferably greater than about 1.5 ft-lb/in.

5 A particularly preferred HIPS material available from Mobil under the trade designation Mobil 7100 impact-modified polystyrene. Other useful HIPS materials include Huntsman PS730 rubber modified polystyrene, BASF PS 4600 impact resin, and Dow Styron 484 HIPS.

The third essential component of the inventive adhesive blend is a functionalized styrene-ethylene/butylene-styrene (SEBS) block copolymer, which comprises an SEBS backbone modified with acid or derivative functional groups.

10 The SEBS backbone can be described as a partially hydrogenated styrene-butadiene-styrene polymer or, alternatively, a block copolymer of styrene and an aliphatic middle block, preferably, an "ABA" copolymer in which the "A" blocks are polystyrene and the "B" or middle block is an aliphatic polymer such as homopolymers or copolymers of butadiene, hydrogenated butadiene, isoprene, or hydrogenated isoprene. Such copolymers typically contain from about 20 wt.% to about 40 wt.% polystyrene end blocks and from about 60 wt.% to about 80 wt.% of the middle block.

15 The functionalized SEBS block copolymer is preferably an SEBS block copolymer grafted with an acid compound or derivative grafting monomer, such as an ethylenically unsaturated carboxylic acid, anhydride, or other derivative. Grafting may be effected by blending the grafting monomer and the block copolymer in an extruder or other mixer or in solvent dispersion, along with a reaction initiator, such as an organic peroxide.

Typically, the grafted block copolymer comprises up from about 0.02 wt.% to about 20 wt.%, preferably about 0.1 wt.% to about 10 wt.%, and highly preferably about 0.2 wt.% to about 5 wt.% grafted monomer. Functionalized block copolymers containing about 1 wt.% to about 2 wt.% grafted maleic anhydride grafting monomer are preferred. Such materials are commercially available from Shell Chemical Company under the trade designation Kraton® FG copolymers. A particularly preferred functionalized SEBS copolymer is Kraton® FG 1901X maleated rubber containing about 2 wt.% grafted maleic anhydride (measured as succinic anhydride groups). Kraton® FG 1921X grafted thermoplastic rubber is also believed to be a commercially available useful material.

25 Kraton® FG 1901X grafted thermoplastic rubber is believed to contain about 28 wt.% styrene and about 72% ethylene/butylene rubber.

Useful functionalized SEBS copolymer materials (including grafting monomers and backbone polymers) and methods for the preparation thereof are further described in Pucci et al. U.S. Patent No. 5,070,143 (December 3, 1991) and Gergen et al. U.S. Patent No. 4,578,429 (March 25, 1986), the respective disclosures of which are hereby incorporated by reference.

The adhesive blends of the invention may be prepared by physically mixing the three essential components plus any additional components or additives by any convenient means. Mixing in a Banbury mixer is an especially convenient preparation method.

35 Typically, the adhesive blends will contain (on a three-component basis) about 40 wt.% to about 99 wt.% ethylene/ester copolymer, about 1 wt.% to about 60 wt.% polystyrene component, and about 0.5 wt.% to about 25 wt.% functionalized SEBS copolymer. Preferably, the adhesive blends will comprise about 60 wt.% to 80 wt.% ethylene/ester copolymer, about 20 wt.% to about 40 wt.% ungrafted polystyrene, and about 4 wt.% to about 16 wt.% functionalized SEBS rubber. A particularly preferred adhesive blend comprises about 68 wt.% EVA containing about 28 wt.% vinyl acetate, about 22 wt.% HIPS, and about 10 wt.% Kraton® FG 1901X maleated rubber, along with an antioxidant package.

40 The blends of the invention find utility in forming composite structures by adhering a layer of the adhesive to one or more substrates by any convenient means, and by coextrusion in particular. Substrates of particular interest include non-polar polyolefins such as low density polyethylene (LDPE), for example, polar substrates such as ethylene vinyl alcohol (EVOH), for example, and any of the wide variety of styrene polymers, including homopolymers and copolymers. 45 The styrene polymers may but need not necessarily be modified by the inclusion of an elastomer. Impact-modified polystyrene substrates are of particular interest due to their utility as structural layers in multilayer laminate structures. Useful substrates include those formed from the family of styrene-butadiene copolymers sold under the trade designation "K-Resin" by Phillips 66 Company.

One advantage of the invention is its excellent adhesion under a variety of conditions to non-polar polyolefins, polar polymers and other polar substrates, polystyrene substrates, and to polyethylene (e.g., LLDPE, VLDPE, LDPE, MDPE, and HDPE), EVOH, and HIPS substrates in particular. The composite structures are easily formed, and can be readily die cut even after thermoforming. Each of the constituents of the adhesive blend is approved by the U.S. FDA and the European Economic Community regulations regarding suitability for use in food packaging.

50 Composite structures of the invention, and particularly those of the structure LDPE/adhesive/EVOH/adhesive/HIPS find great utility in the fabrication of refrigerator liners and food packaging such as thermoformed cups, flexible sheets, cast or blown films, cast sheets, etc. 55

**EXAMPLES**

The following non-limiting examples are intended to illustrate the practice of the invention and comparison with other adhesive blends used in composite structures.

**Example 1**

As set forth in Table 1 below, a series of inventive adhesive blends designated A-I were prepared by mixing the identified components in the indicated proportions in a laboratory Brabender mixer. The Brabender process conditions included a shot weight of 40 g, a temperature of 420°F, mixer speed of 100 rpm, and mixing time of three minutes. The commercial source of each component is indicated in parentheses along with its trade designation.

Additionally, a comparative blend 1 comprising 25 wt.% Mobil 7100 impact-modified polystyrene, 67 wt.% Quantum UE 634-04 EVA, and 8 wt.% of a high density polyethylene homopolymer grafted with about 2 wt.% maleic anhydride was prepared under the same conditions.

A comparative blend 2 comprised DuPont Bynel® E359 anhydride-modified ethylene vinyl acetate having a melt index of about 4.3 g/10 min. according to ASTM D-1238 (190°F, 2.16 g). This material is disclosed to be adhesive to polystyrenes, ethylene vinyl alcohol, and polyethylenes, is advertised to be well suited to structures such as polystyrene/adhesive/EVOH/adhesive/polyethylene.

All percentages are given in terms of weight.

TABLE 1

INVENTIVE COMPOSITIONS									
MATERIAL	A	B	C	D	E	F	G	H	I
HIPS (Mobil 7100)	25%	20%	20%	30%	30%	35%	30%	50%	22%
EVA (QUAN- TUM UE 634-04)	67%	68%	72%	64%	62%	57%	58%	42%	68%
KRATON® FG1901X (SHELL)	8%	12%	8%	6%	8%	8%	12%	8%	10%
IRGANOX 1010 Anti- oxidant	1000 PPM	1000 PPM	1000 PPM	1000 PPM	1000 PPM	1000 PPM	1000 PPM	1000 PPM	1000 PPM

Each of the compositions was tested for heat seal adhesion strength using a Sentinel heat sealer with a 1 inch seal bar width. Testing was conducted at 350°F, 400°F, and 450°F. (Heat seal data obtained at 400°F are generally considered to best correlate to results obtained under coextrusion conditions.)

Each adhesive was sealed against substrates of ethylene-vinyl alcohol copolymer (EVAL® F101 obtained from Kuraray), LDPE (Quantum NA 212), and HIPS (Mobil 7100). Adhesion was measured in terms of 180° T-peel adhesion strength in lb/in. Results are given in Table 2, below.

TABLE 2

HEAT SEAL ADHESION STRENGTH T-PEEL ADHESION STRENGTH (LB/INCH)									
350°F Heat Seal Temp.			400°F Heat Seal Temp.			450°F Heat Seal Temp.			
Material	EVOH (EVAL F101)	LDPE QUANTUM NA 212)	HIPS (MOBIL 7100)	EVOH (EVAL F101)	LDPE (QUAN- TUM NA 212)	HIPS (MOBIL 7100)	EVOH (EVAL F101)	LDPE (QUAN- TUM 212)	HIPS (MOBIL 7100)
A	2.5	2.2	2.0	3.4	2.4	2.1	3.4	3.1	2.1
B	2.4	2.7	2.2	3.5	2.8	2.3	3.4	4.3	2.3
C	0.8	2.8	2.1	4.2	2.8	1.9	3.3	4.0	2.1
D	1.3	2.6	1.6	3.2	2.4	1.7	3.4	2.9	1.4
E	1.2	2.6	1.6	3.2	2.4	1.7	3.4	2.8	1.5
F	1.6	2.4	1.2	3.5	2.5	1.4	3.5	2.7	1.2
G	1.5	2.2	1.4	3.3	2.7	1.6	3.8	3.1	1.6
H	0.8	1.5	0.8	3.3	2.2	0.8	3.6	4.0	0.9
I	1.7	2.5	1.9	3.5	2.7	2.2	3.3	4.0	2.0
1	3.1	3.6	1.2	2.8	3.0	1.0	3.1	3.3	1.1
2	3.6	4.2	1.4	4.8	4.4	1.3	4.2	5.4	1.3

In composites comprising multiple diverse substrates, the overall adhesive strength of the composite structure is evaluated with respect to the weakest adhesion value present in the composite. A review of the foregoing reveals that the inventive adhesive blends give excellent adhesion to each of the three tested diverse substrates over a wide range of temperature and compositional characteristics.

#### Example 2

Table 3 below provides a summary of the compositions of three inventive blends J-L.

TABLE 3

INVENTIVE COMPOSITIONS			
Material	J	K	L
HIPS (HUNTSMAN PS730)	22%	20%	
HIPS (BASF PS 4600)			20%
EVA (QUANTUM UE 634-09)	68%	68%	68%
KRATON® FG 1901X (SHELL)	10%	12%	12%
IRGANOX 1010 Antioxidant	1000 PPM	1000 PPM	1000 PPM

Each of the inventive adhesive J-L and comparative adhesive 2 was coextruded with HIPS, EVOH, and LDPE into sheets having the structure shown below with thickness given in miles:

HIPS/ADHESIVE/EVOH/ADHESIVE/LDPE					
54	0.75	1.5	0.75	4.0	MIL

Each sheet was tested for 90° and/or 180° T-peel adhesion strengths in the machine direction (MD) and transverse direction (TD) after five and 17 days using a sheet width of 1 inch and a T-peel speed of 10 inches per minute. Results are shown in Table 4, below.

The sheets described above were formed into thermoformed cups of the structure shown below, with thickness given in mils:

HIPS/ADHESIVE/EVOH/ADHESIVE/LDPE					
16.0	0.25	0.50	0.25	1.25	MIL

180° T-peel strength was tested after two days using ½ inch sample width and T-peel speed of 10 inches per minute. Results were shown in Table 4, below.

TABLE 4

COEXTRUSION ADHESION STRENGTH (LB/IN.)			
Material	COEXTRUDED SHEET (MD)	COEXTRUDED SHEET (TD)	THERMOFORMED CUP
J	3.4 5 DAYS HIPS SEPARATION	3.2 5 DAYS HIPS SEPARATION	0.9 2 DAYS HIPS SEPARATION
90 DEGREE T-PEEL	3.2 17 DAYS HIPS SEPARATION	4.3 17 DAYS HIPS SEPARATION	
	5.5 17 DAYS HIPS SEPARATION	6.2 17 DAYS HIPS SEPARATION	
K	2.7 5 DAYS HIPS SEPARATION	4.0 5 DAYS HIPS SEPARATION	0.9 2 DAYS HIPS SEPARATION
L	3.1 5 DAYS HIPS SEPARATION	3.2 5 DAYS HIPS SEPARATION	0.8 2 DAYS HIPS SEPARATION
2	6.3 C 5 DAYS EVOH SEPARATION	2.8 5 DAYS HIPS SEPARATION	0.8 C 2 DAYS HIPS SEPARATION
90 DEGREE T-PEEL	6.2 C 17 DAYS EVOH SEPARATION	2.7 17 DAYS HIPS SEPARATION	
	7.9 C 17 DAYS EVOH SEPARATION	3.8 17 DAYS HIPS SEPARATION	
C = COHESIVE FAILURE OF ADHESIVE DURING T-PEEL			

In each of the inventive and comparative blends, no elongation strings appeared during thermoforming.

The results shown in Table 4 illustrate that the inventive blends are characterized by uniform adhesion values in both the machine direction and the transverse direction in finished thermoformed products. Adhesion values at least as

high as three of the comparison material were maintained during thermoforming, despite higher initial adhesion in one direction in the comparative blend. Therefore, the foregoing demonstrates the capability of blends of the invention to avoid or minimize loss of both 90° and 180° T-peel adhesion strength under thermoforming conditions.

The foregoing detailed description is given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications within the scope of the invention may be apparent to those skilled in the art.

### Claims

1. An adhesive blend, comprising a mixture of:
  - (a) an ethylene/ester copolymer;
  - (b) polystyrene; and
  - (c) a functionalized SEBS block copolymer.
2. The adhesive blend of claim 1 wherein said ethylene/ester copolymer is selected from the group consisting of ethylene/vinyl acetate copolymers and ethylene/acrylate copolymers.
3. The adhesive blend of claim 1 wherein said ethylene/ester copolymer is an ethylene/vinyl acetate copolymer having a vinyl acetate content in the range of about 5 wt.% to about 40wt.%.
4. The adhesive blend of anyone of claims 1-3 wherein said polystyrene is impact-modified polystyrene having a melt index according to ASTM D-1238, Condition G in the range of about 0.5 g/10 min to about 12 g/10 min.
5. The adhesive blend of claim 4 wherein said impact-modified polystyrene has a notched Izod impact value at 73°F according to ASTM D-256 of greater than about 0.5 ft-lb/in.
6. The adhesive blend of claim 5 wherein said notched Izod impact value is greater than about 1.5 ft-lb/in.
7. The adhesive blend of anyone of claims 1-6 wherein said SEBS block copolymer of (c) is functionalized by grafting with an acid compound or derivative grafting monomer.
8. The adhesive blend of claim 7 wherein said functionalized SEBS block copolymer of (c) contains about 0.2 wt.% to about 20 wt.% bound grafting monomer.
9. The adhesive blend of claim 8 wherein said bound grafting monomer comprises about 0.01 wt.% to about 10 wt.% of said functionalized SEBS block copolymer of (c).
10. The adhesive blend of claim 9 wherein said bound grafting monomer comprises about 0.02 wt.% to about 5 wt.% of said functionalized SEBS block copolymer of (c).
11. The adhesive blend of anyone of claims 7-10 wherein said grafting monomer is maleic anhydride.
12. The adhesive blend of claim 11 wherein said functionalized SEBS block copolymer has a styrene-to-rubber weight ratio of about 28:72 comprises about 2 wt.% grafted maleic anhydride.
13. The adhesive blend of anyone of claims 1-12 wherein said ethylene/ester copolymer of (a) comprises about 40 wt.% to about 99 wt.% of said blend, said polystyrene of (b) is high impact polystyrene (HIPS) and comprises about 1 wt.% to about 60 wt.% of said blend, and said functionalized SEBS block copolymer of (c) comprises about 0.5 wt.% to about 25 wt.% of said blend.
14. The adhesive blend of claims 13 wherein said ethylene/ester copolymer of (a) comprises about 60 wt.% to about 80 wt.% of said blend, said HIPS of (b) comprises about 20 wt.% to about 40 wt.% of said blend, and said functionalized SEBS block copolymer of (c) comprises about 4 wt.% to about 16 wt.% of said blend.
15. The adhesive blend of claim 13 or 14 wherein said copolymer of (a) is an ethylene/vinyl acetate copolymer having a vinyl acetate content of 28 wt.% and comprises about 22 wt.% of said blend, and said functionalized SEBS block copolymer of (c) comprises about 10 wt.% of said blend.

16. The adhesive blend of anyone of claims 1-15 wherein said functionalized SEBS block copolymer of (c) is that sold under the trade designation Kraton® FG 1901X.

17. A composite structure comprising the adhesive blend of claim 1 adhered to a substrate.

18. The composite structure of claim 17 wherein said substrate is formed from a material selected from the group consisting of non-polar polyolefins, polar substrates, and polystyrene.

19. The composite structure of claim 18 wherein said material is selected from the group consisting of linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), low density polyethylene (LDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), ethylene vinyl alcohol copolymers (EVOH), and impact-modified polystyrene.

20. The composite structure of claim 18 comprising PE/adhesive/EVOH/adhesive/HIPS wherein PE is polyethylene selected from the group consisting of LLDPE, VLDPE, LDPE, MDPE, HDPE, and blends thereof, and the adhesive in each case is an adhesive blend of claim 1.

21. The composite structure of claim 20 comprising LDPE/adhesive/EVOH/adhesive/HIPS.

22. The composite structure of anyone of claims 17-21 formed by coextrusion.

23. The composite structure of claim 22 in the form of food packaging, a refrigerator liner, cast film, blown film, or cast sheet.

24. The composite structure of claim 23 in the form of a thermoformed cup or flexible packaging for meat or cheese.





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## EUROPEAN SEARCH REPORT

Application Number  
EP 95 11 8248

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP-A-0 412 503 (MITSUI PETROCHEMICAL) * page 3, line 25 - page 6, line 10 *	1-24	C09J123/08
A	US-A-4 861 677 (I-H.LEE) * column 2, line 21 - column 4, line 6 *	1-24	
A	DE-A-27 03 078 (BASF) * page 3, paragraph 4 - page 7, paragraph 1 *	1-24	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C09J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 4 March 1996	Examiner Schmidt, H
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

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